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# Discriminating Gasoline Fuel Contamination in Engine Oil by Terahertz Time-Domain Spectroscopy

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## Abstract

Gasoline engine oil (SAE 5W20) was contaminated with four levels (0%, 4%, 8% and 12%) of gasoline fuel and submitted to terahertz time-domain spectroscopy (THz-TDS). Three sampling methods were used to compare measurement variations. For all sampling methods, refractive index decreased with increased fuel contamination and absorption coefficient increased with increased fuel contamination. Absorption coefficients were significantly different for each fuel contamination level for each sampling method across the entire 0.5-2.5 THz range. The frequency of 0.5 THz produced the best model of absorption coefficient predicting fuel contamination with a root-mean-square error of 0.21 percentage points. THz-TDS demonstrated high potential for estimating gasoline fuel contamination in gasoline engine oil.

**Keywords:** terahertz spectroscopy; engine lubrication oil; oil condition; gasoline fuel contamination

## Acknowledgements

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## 1. Introduction

Many new automobiles include some indicator for when to change engine oil. These indicators tend to be based on mileage or elapsed time since the last exchange only or may include some operating condition data (*e.g.* oil temperature). Unfortunately, these indicators have not been developed to alert operators about critical engine oil contamination levels that could result in engine damage. Gasoline contamination is one major concern for engine oil monitoring of gasoline-powered vehicles.

Gasoline contaminates engine oil as unburned fuel runs down the cylinder walls, leaks past the piston rings, and washes away [1] and intermixes with the lubricating oil [2]. This fuel-oil

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4 mixing increases with combustion chamber pressure, fuel mixture ratio, and decreasing cylinder  
5 temperature [2]. Some minimal fuel contamination may occur at engine startup and before an  
6 engine reaches normal operating temperature. Moderate fuel contamination occurs when an  
7 engines operates with an overly rich fuel-air ratio due to poor adjustment or a faulty sensor.  
8 More serious fuel contamination occurs when a fuel delivery component fails allowing excessive  
9 fuel into an engine, resulting in a relatively high level of fuel contamination of engine oil. The  
10 effects of gasoline dilution of lubricating oil include: oil viscosity reduction [3, 4, 5], accelerated  
11 oil oxidation [6, 7], and sludge inside the engine [2, 4].  
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15 Excessive levels of gasoline contamination in engine oil reduce oil viscosity and risk engine  
16 damage. Gasoline fuel contamination of 5% in engine oil has been reported as a warning limit  
17 [8] or oil change indicator [9]. A significant decrease in oil viscosity has been caused by 2.5%  
18 fuel dilution of lubricating oil [10]. Contamination of 5-10% gasoline in engine oil can result in a  
19 50% viscosity reduction (at 40°C) [11]. Oil contamination of 9% gasoline resulted in a 30%  
20 reduction in viscosity [9].  
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23 Researchers have attempted to find methods for sensing gasoline in engine oil that could lead to  
24 an *in situ* or on-site sensor system. Infrared has been studied [12, 13], but in most cases a  
25 viscosity sensor was used to detect viscosity changes, that would include reductions caused by  
26 gasoline contamination [14, 15, 16, 17, 10, 18]. As new sensor concepts or spectroscopy methods  
27 are developed, they are often evaluated for new applications. Terahertz (THz; 100 GHz-10 THz)  
28 spectroscopy is an example of a newer technology for which many potential applications have  
29 been identified [19, 20]. Prior research using THz-time-domain spectroscopy (THz-TDS) to  
30 distinguish among petroleum and related products or contaminants includes: mineral oil with  
31 additives [21], three grades of gasoline [22], engine oils with and without additives [23], six  
32 grades of lubricating oil [24], oil base stock and additive [25], gasoline and diesel fuel [26],  
33 ethanol and gasoline mixtures [27], three grades of gasoline engine oil [28], water in diesel  
34 engine oil [29], and sulfur in gasoline and methyl methacrylate in diesel fuel [30].  
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### 39 **1.1. Objectives**

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41 The objective of this study was to assess the ability of THz-TDS to identify four levels of fuel  
42 contamination (0%, 4%, 8%, and 12%) of gasoline engine oil (SAE 5W-20) using two sampling  
43 methods for THz-TDS. The first method focused on the potential of THz-TDS assuming  
44 homogeneity of samples and highly repeatable sampling and measurement procedures and used  
45 one cuvette preparation per contaminant level with three consecutive THz-TDS measurements.  
46 The second method explored reproducibility and consistency of the results by preparation of five  
47 separate cuvettes from each oil contamination level sample with one THz measurement per  
48 cuvette, mimicking real-life applications with variations among different measurement setup  
49 configurations. A third method, which was a variant of the second method, used delta values  
50 based on subtracting the non-contaminated (0%) sample value from each contaminated sample  
51 value. This third method would be a better approximation for a fixed setup that could be installed  
52 in an engine in which a fresh oil sample was measured as an initial reference and then the same  
53 oil was measured after various periods of use, but does not account for variation among THz  
54 setups.  
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## 59 **2. Materials and Methods**

## 2.1. Oil Sample Preparation

A 4.73 L container of Pennzoil SAE 5W-20 (API SN service category) gasoline engine oil was purchased at a retail local store in Carbondale, Illinois, USA. The SAE 5W-20 grade was chosen because it was commonly specified by automobile manufacturers for gasoline engines. Each sample of 0%, 4%, 8%, and 12% (v/v %) gasoline contamination was prepared by using a graduated syringe to remove 50 ml of fresh engine oil from the original container and place it in a 60 ml amber Boston round glass container (Qorpak GLC-01909, Fisher Scientific). For the gasoline contaminated samples, a pipette was used to remove 2 ml, 4 ml, and 6 ml of fresh oil, respectively from the 4%, 8%, and 12% samples and replace with the same volume of gasoline. The gasoline was 87 octane fuel obtained from a local gas station. Sample containers were sealed with a phenolic polycarbonate lined cap and shaken by hand for 60 seconds. The sample bottles were labeled and shipped to Technische Universität Darmstadt, Germany for THz-TDS analysis. All samples were assumed to be homogeneous, based on visual observation. Fuel evaporation was minimized by sealing containers, storing away from sunlight at room temperature, and shipping to Germany during cooler January temperatures.

## 2.2. THz-TDS Spectrometer

The THz-TDS spectrometer shown in Fig. 1 consisted of a commercial system from MenloSystems GmbH that used a 1550 nm pulsed laser with a pulse length shorter than 90 fs and a pair of fiber coupled photoconductive antennas (PC) as source and detector. The entire THz path was encapsulated and purged with dry nitrogen in order to eliminate water vapor traces from the measurement. The system permitted real time data acquisition (6 spectra /s) with a single shot bandwidth of about 1 THz. The noise floor was dominated by shot noise of the detector which was reduced by averaging individual traces. Therefore, spectra were averaged over either 200 s or 500 s, yielding a maximum (usable) bandwidth of about 4 THz as shown in Fig. 2. The choice of these averaging times was a compromise between measurement time and bandwidth. Since the dynamic range fell off quickly above 2-3 THz, longer averaging only allowed for marginal improvement of the bandwidth. With 500 s averages, the dynamic range at the peak frequency of 0.27 THz was 90 dB and decreased with increasing frequency until it reached the noise floor. All measurements were done in a transmission configuration using a collimated THz beam transmitted through a cuvette containing the oils. The cuvette consisted of 3 mm thick polyethylene (PE) windows separated by a metal spacer. Two metal spacers allowed 3 different THz path lengths: 5, 10, and 15 mm. An outer metal frame firmly locked the windows ensuring the straightness of the windows and a well defined and reproduceable size of the probe volume. From the reflection echo of the cuvette windows ( $R_C$  in Fig. 2a) we determined the standard deviation of the THz path length in the cuvette,  $d_C$ , due to assembly/disassembly and tilt errors of the cuvette of only 10  $\mu\text{m}$ .

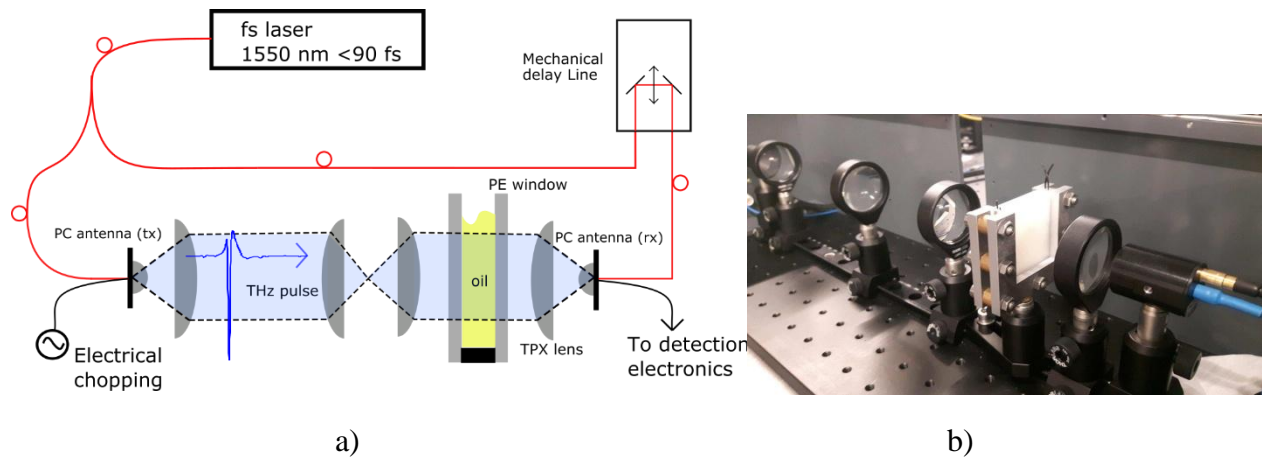


Figure 1. (a) Schematic of the THz time-domain spectrometer. (b) Image of the THz path including the cuvette.

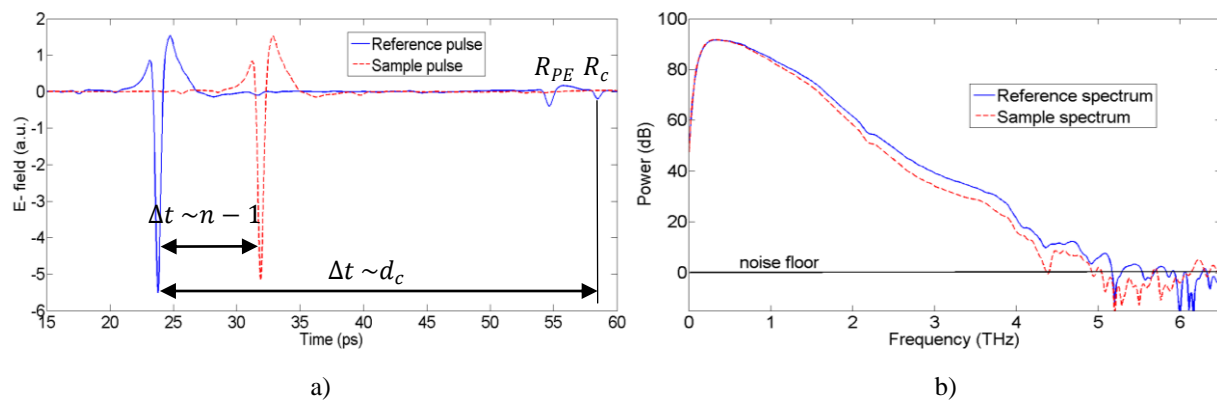


Figure 2. (a) Time and (b) frequency domain representation of the pulse obtained with the empty cuvette with a 5 mm spacer (blue solid trace) that served as reference spectrum for the measurement and filled with the oil sample (red dashed trace). From the reference spectrum it was possible to accurately determine the cuvette path length by identifying the internal reflection ( $R_C$ ) between the two PE windows. The third peak ( $R_{PE}$ ) was due to a Fabry Pórot oscillation within the PE windows. The frequency spectra were obtained only from the information contained in the main peaks by time windowing.

### 2.3. THz-TDS Measurements

Five different sample preparation rounds were performed, using once a 5 mm spacer (cuvette 2), twice a 10 mm spacer (cuvettes 1 and 3) and twice the two spacers together obtaining a distance of 15 mm (cuvettes 4 and 5). The different cuvette sizes were used to estimate systematic errors due to alternations of the THz-TDS setup. Prior work to characterize petroleum and related products has used various cuvette thicknesses, including 2 mm [26, 27], 5.9 mm [28, 29], 10 mm [22, 25, 30], and 15 mm [24]. The second 15 mm preparation of this study was exposed three consecutive times, removing and reinserting the sample into the system in order to identify the

error originating from sample positioning and system stochastic errors. At each round, all four samples were characterized through a reference and sample measurement (Fig. 2). Gasoline mixed sample bottles were shaken well in order to ensure a good mixing of its components. In order to allow for air bubbles to leave the mixtures, the samples were kept at rest over night before measurements were taken. This waiting time should only have a minor influence on demixing. For most measurements, the spectra were averaged over 500 s. Only in the last round, where 3 consecutive measurements were taken, the averaging time was 200 s, without any noticeable effect in the frequency range of interest (0.5 - 2.5 THz) and still showed 20 dB dynamic range at 2.5 THz even for the most absorptive samples.

By postprocessing, the effect of reflections was removed. The PE windows were thick enough to ensure no overlap of the reflected pulse with the main pulse. From the reflection-free data, the refractive index,  $n_s$ , was obtained by extracting the phase shift of the Fourier transform of reference and sample measurements by

$$n_s(f) = 1 - \frac{c_0}{2\pi f d_c} (\varphi_S(f) - \varphi_R(f)) \quad (1)$$

with  $\varphi_S(f)$  and  $\varphi_R(f)$  the Fourier phases of the sample measurement and reference measurement, respectively,  $c_0$  the vacuum speed of light, and  $d_c$  the probe volume length. The absorption coefficient,  $\alpha$ , can then be found by [31]

$$\alpha(f) = -\frac{2}{d_c} \ln \left( t(f) \frac{(n_s(f) + n_w)^2}{(1 + n_w)^2 n_s(f)} \right) \quad (2)$$

where  $f$  is the frequency,  $d_c$  is the sample thickness,  $n_s(f)$  is the refractive index of the sample at frequency  $f$ ,  $n_w$  is the refractive index of the window and  $t(f)$  is the transmission ratio of the amplitude between sample and reference measurements at the given frequency.

The previously mentioned 10  $\mu\text{m}$  path length error, resulted in an error of the refractive index and absorption coefficient values. The equations to approximate the error in refractive index ( $\Delta n$ ) and absorption coefficient ( $\Delta \alpha$ ) were

$$\Delta n \approx (n - 1) \frac{\Delta d}{d_c} \quad (3)$$

$$\Delta \alpha \approx \left( \alpha - \frac{2}{d_c} \ln \left( \frac{(n + n_w)^2}{n(1 + n_w)^2} \right) \right) \frac{\Delta d}{d_c} + 2 \left( \frac{2(n-1)(n+n_w)}{n(1+n_w)^2} + 1 \right) \frac{\Delta d}{d_c^2} \quad (4)$$

where  $d_c$  is the measured thickness,  $\Delta d$  is the thickness error,  $n_w$  is the refractive index of the windows and  $n$  and  $\alpha$  are the measured values. Measurement error increased with decreased sample thickness and was calculated to be 0.06% for refractive index and 1.75% for absorption coefficient for the 5 mm sample thicknesses compared to 0.02% for refractive index and 0.26% for absorption coefficient for the 15 mm sample thickness.

## 2.4. Data Analysis

Analysis of variance (ANOVA) was used to determine if there were significant differences among the fuel contamination levels at each frequency for both refractive index and absorption

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4 coefficient. The alpha level for significance was 0.05. For the sampling method using a single  
5 cuvette for each sample, each of the three consecutive THz measurements was a replication for  
6 analysis purposes. For the sampling method with five separate cuvettes per sample, a  
7 measurement from each cuvette was a replication for analysis purposes. The descriptive statistics  
8 of mean, standard deviation, and 95% confidence interval of the refractive index and absorption  
9 coefficient of each frequency were calculated for each fuel contamination level. Mean values and  
10 standard deviations of refractive index and absorption coefficient at 1.0 THz were reported for  
11 comparison with other studies.  
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15 Regression analysis was used to determine a linear trend for the frequency range from 0.5-2.50  
16 THz at an interval of 0.25 THz [32, 28, 29]. The regression was based on a limited dataset and  
17 the aim was a preliminary estimate of fuel contamination by using the best frequency from  
18 refractive index or absorption coefficient data. The coefficient of determination ( $R^2$ ) was used to  
19 determine the best frequency and model to predict the fuel contamination. Root-mean-square  
20 error (RMSE) was reported as the measure of differences between predicted and actual values.  
21 SAS Enterprise Guide 7.1 software [33] was used for ANOVA, Fisher's LSD test, and regression  
22 analysis.  
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### 25 26 **3. Results and Discussion**

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28 THz-TDS was used to obtain refractive index and absorption coefficient data for the gasoline  
29 contaminated oil samples. Frequencies in the range of 0.5-2.5 THz were used for analysis. The  
30 frequency resolution was approximately 7 GHz.  
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#### 32 33 **3.1. Single Cuvette with Three Consecutive Measurements**

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35 The first sampling method consisted of preparing a single cuvette (15mm path length) for each  
36 oil sample and then making three consecutive measurements with THz-TDS in order to analyze  
37 statistical errors and the influence of statistic fluctuations (power, noise) within the setup. This  
38 method provides the best indicator of THz-TDS potential assuming homogeneity of samples and  
39 absolute repeatability of sampling and measurement procedures with a fixed setup in a  
40 laboratory-scale environment.  
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##### 43 44 **3.1.1. Refractive Index**

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46 The refractive indices for the four levels (0%, 4%, 8%, and 12%) of gasoline contaminated  
47 engine oil samples were illustrated in Fig. 3. The refractive indices decreased slightly as  
48 frequency increased and the differences among the samples increased as gasoline contamination  
49 increased. The mean refractive indices at 1.0 THz for the 0%, 4%, 8%, and 12% samples were  
50 1.4666, 1.4657, 1.4645, and 1.4626, respectively with standard deviations less than 0.00002.  
51 Variations in refractive index across the range of 0.5-2.5 THz were 0.0015, 0.0029, 0.0041, and  
52 0.0053, respectively. The 0% sample can be compared to another study that used the same oil,  
53 but with different THz-TDS equipment. In that experiment, the refractive index at 1.0 THz was  
54  $1.4610 \pm 0.0009$  ( $\pm$  standard deviation), with a maximum variation of 0.0012 across the 0.5-2.0  
55 THz range [28]. The refractive index curve of the same oil in the prior experiment was relatively  
56 flatter. The difference in refractive indices between the studies was attributed to differences  
57 between the spectrometer configurations and variations between batches of the same oil. Since  
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any variations among oil batches was unknown the differences resulting solely from the spectrometer configurations were unknown.

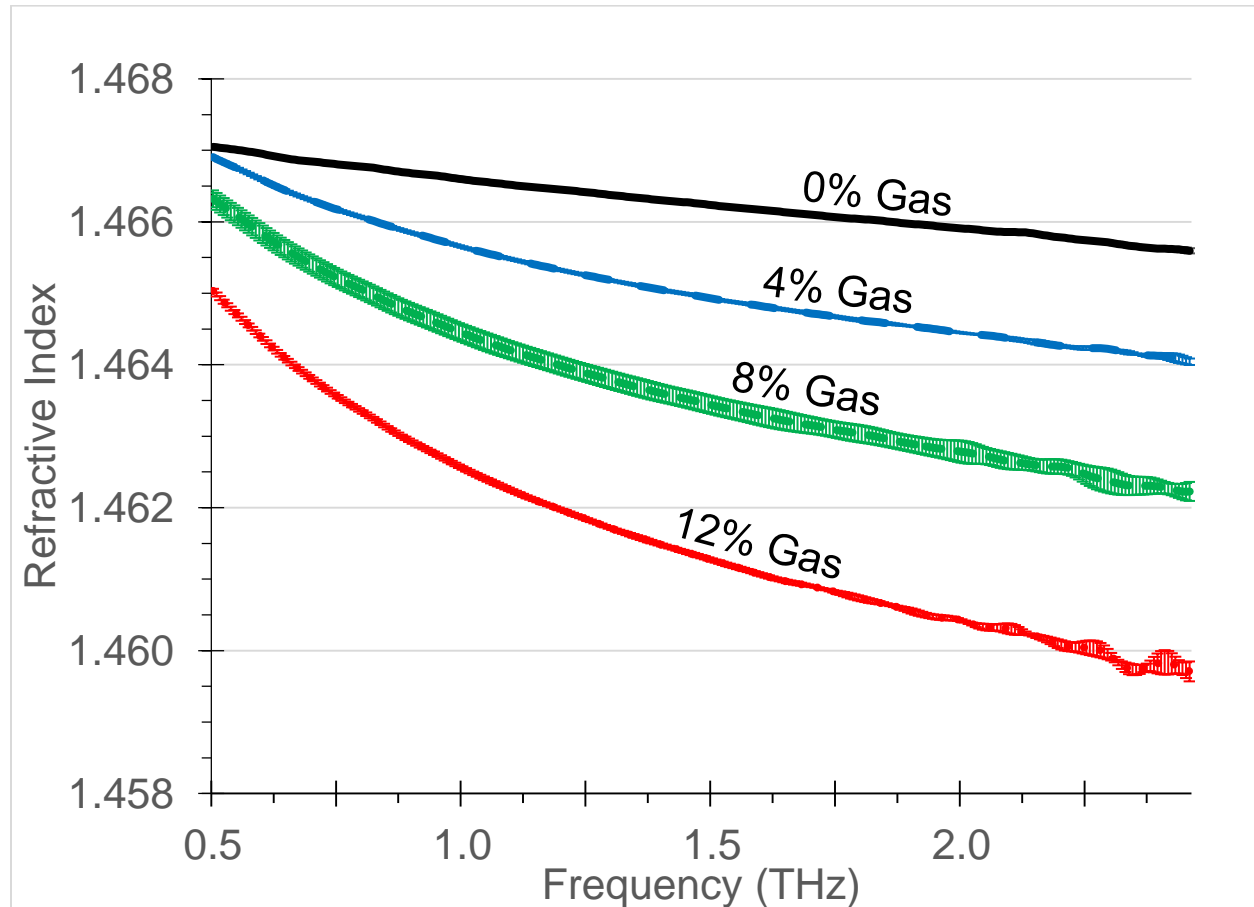


Figure 3. Mean refractive index from three measurements of one cuvette of gasoline engine oil (SAE 5W-20) samples with four levels of fuel contamination with 95% confidence interval bars.

There was noticeable spacing among the gasoline contamination levels and the relatively short 95% confidence bars indicated high repeatability among THz measurements and high discrimination among the samples. The ANOVA analysis resulted in highly significant differences ( $p < 0.0001$ ) among refractive index for the gasoline contaminant levels across the 0.5-2.5 THz range. Based on Fisher's LSD method, there were significant differences between each contamination level. Refractive index decreased as gasoline contamination increased. This decrease in refractive index was consistent with the lower refractive index of gasoline, which has ranged from 1.407-1.448 [22, 26, 34, 35]. Higher concentrations of gasoline contamination would be expected to have lower refractive indices.

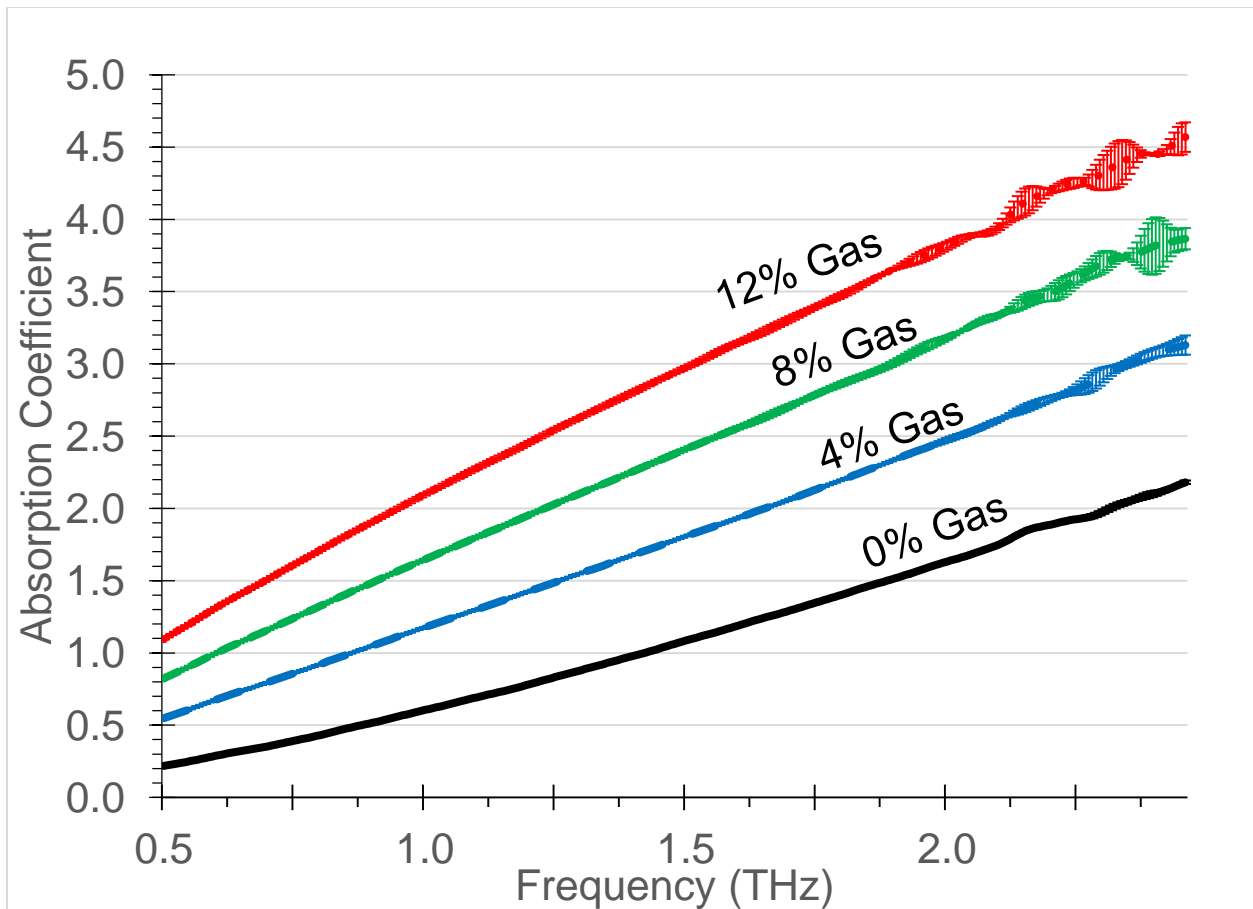
The observed measurement variation, based on standard deviation, was 0.0006%, 0.0007%, 0.0073%, and 0.0015% for the 0%, 4%, 8%, and 12% samples, respectively, at 1 THz. This does not reflect thickness measurement variation of 0.02% for the 15 mm cuvettes, since the cuvette was not disassembled between measurements. The high repeatability of THz measurements



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4 indicates the potential of a single THz-TDS setup with a fixed cuvette to differentiate gasoline  
5 contamination levels in engine oil.  
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### 7 8 **3.1.2. Absorption Coefficient** 9

10 The absorption coefficients of the four levels of fuel contamination in the gasoline engine oil  
11 were illustrated in Fig. 4. Each of the four gasoline contamination levels exhibited a similar  
12 pattern as absorption coefficient increased approximately linearly with frequency. Each curve  
13 was distinct from the other with slight increase in separation with increasing frequency. The  
14 mean absorption coefficients at 1.0 THz for the 0%, 4%, 8%, and 12% samples were 0.599,  
15 1.169, 1.636, and 2.084, respectively with standard deviations of up to 0.009. The non-  
16 contaminated sample (0%) had a mean absorption coefficient from 0.218-1.591 across the 0.5-  
17 2.0 THz range with further increase to 2.181 from 2.0-2.5 THz. This compared with an  
18 absorption coefficient increase from 0.176-1.34 across the 0.5-2.0 THz range for a prior study  
19 with the same manufacturer and grade of oil [28]. As with refractive index, differences in the  
20 measurements between studies can be attributed to differences in the batches of oil and different  
21 spectrometer configurations.  
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57 Figure 4. Mean absorption coefficient from three measurements of one cuvette of gasoline  
58 engine oil (SAE 5W-20) samples with four levels of fuel contamination with 95% confidence  
59 interval bars.  
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4 There was noticeable spacing among the gasoline contamination levels and the relatively short  
5 95% confidence bars indicated high repeatability among THz measurements and high  
6 discrimination among the samples. The ANOVA analysis resulted in highly significant  
7 differences ( $p < 0.0001$ ) for absorption coefficient among the gasoline contaminant levels across  
8 the 0.5-2.5 THz range. Based on Fisher's LSD method, there were significant differences  
9 between each contamination level. The increase in absorption coefficient with frequency is  
10 consistent with studies of gasoline engine oil of SF service category [24] and gasoline [22, 26].  
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14 At 1 THz, the observed measurement variation was 0.06%, 0.1%, 0.2%, and 0.4% for 0%, 4%,  
15 8%, and 12% samples, respectively. Since the cuvette was not disassembled between  
16 measurements these variations are not attributable to sample thickness measurement and are  
17 related to the samples. Regardless, the absorption coefficient curve patterns indicate strong  
18 potential for discrimination among gasoline contamination levels.  
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### 21 **3.1.3 Refractive Index and Absorption Coefficient as Predictors of Gasoline Contamination**

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23 Based on the separation and statistical significance of means of each fuel contamination level for  
24 both refractive indices (Fig 3) and absorption coefficients (Fig. 4) both measures were of interest  
25 for predicting fuel contamination level. Data from nine frequencies (0.5-2.5 THz at 0.25 THz  
26 intervals) were used for linear regression analysis for absorption coefficient. All models were  
27 highly significant ( $p < 0.0001$ ). For refractive index, the  $R^2$  of the linear models ranged from  
28 0.867 at 0.5 THz to a high of 0.987 at 2.5 THz. For absorption coefficient, the  $R^2$  of the models  
29 ranged from a high of 0.998 at 0.5 THz to a low of 0.991 at 2.5 THz. Overall there was little  
30 difference in the fit of the respective models for refractive index ( $n$ ) (Fig. 5a) and absorption  
31 coefficient ( $\alpha$ ) (Fig. 5b). The linear fit equations for fuel contamination at 2.5 THz for refractive  
32 index and 0.5 THz for absorption coefficient to predict fuel contamination were:  
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$$36 \text{ Fuel contamination (\%)} = 2973.8 - 2028.7n \quad (5)$$

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$$38 \text{ Fuel contamination (\%)} = -3.2135 + 13.719\alpha \quad (6)$$

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41 While these equations estimated the relationships of THz-TDS measurements to fuel  
42 contamination, it should be noted that these are only preliminary estimates. Inserting the  
43 measured values into the linear models of Eqs. 5 and 6 yielded a RMSE of 0.51 and 0.21  
44 percentage points, respectively for refractive index and absorption coefficient. These  
45 measurements with prediction errors of fuel contamination well below 1 percentage point show  
46 that a fixed setup is well suited to differentiate between different contamination levels.  
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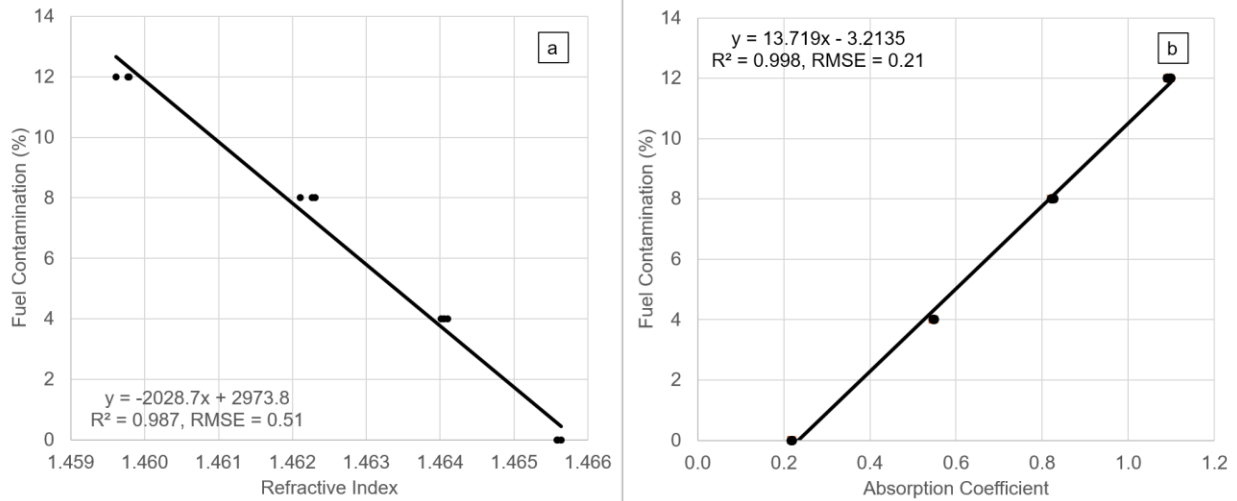


Figure 5. a) Refractive index at 2.5 THz and b) absorption coefficient at 0.5 THz from three measurements of one cuvette predicting fuel contamination with a linear model.

### 3.2. Five Cuvettes with a Single Measurement

This method consisted of preparing five cuvettes of each sample of engine oil contaminated with gasoline (0%, 4%, 8%, and 12%) with one THz-TDS measurement from each cuvette. The five measurements included three different cuvette thicknesses (5 mm, 10 mm, and 15 mm) and two repeated measurements (10 mm and 15 mm), recorded on different days with a different alignment of the THz system in order to characterize potential systematic errors of the measurement technique due to variations in the setup.

#### 3.2.1. Refractive Index

The refractive indices for the four levels (0%, 4%, 8%, and 12%) of gasoline contaminated gasoline engine oil samples were illustrated in Fig. 6. The mean curves were similar to measurements from a single cuvette (Fig. 3) with noticeable spacing between each and ANOVA results indicated significance among the gasoline contamination levels across the entire 0.5-2.5 THz range. The mean refractive indices at 1.0 THz for the 0%, 4%, 8%, and 12% samples were 1.4671, 1.4659, 1.4648, and 1.4632, respectively, with standard deviations less than 0.0013. These mean values at 1.0 THz ranged from 0.0002-0.0004 greater than the corresponding three measurements of the single cuvette. However, the 95% confidence interval bars were much longer and overlapped with adjacent bars from other contamination levels (Fig. 6). Based on Fisher's LSD method, each contamination level was not different from all of the others. The 0% level had a significantly higher refractive index than the 8% and 12% samples across the 0.5-2.5 THz range. Generally, the contamination pairs of 0% and 4% as well as 4% and 8% were not significantly different or distinguishable from each other. The 12% sample was distinguishable across the 0.74-2.5 THz range, as its refractive index was significantly lower than all others.

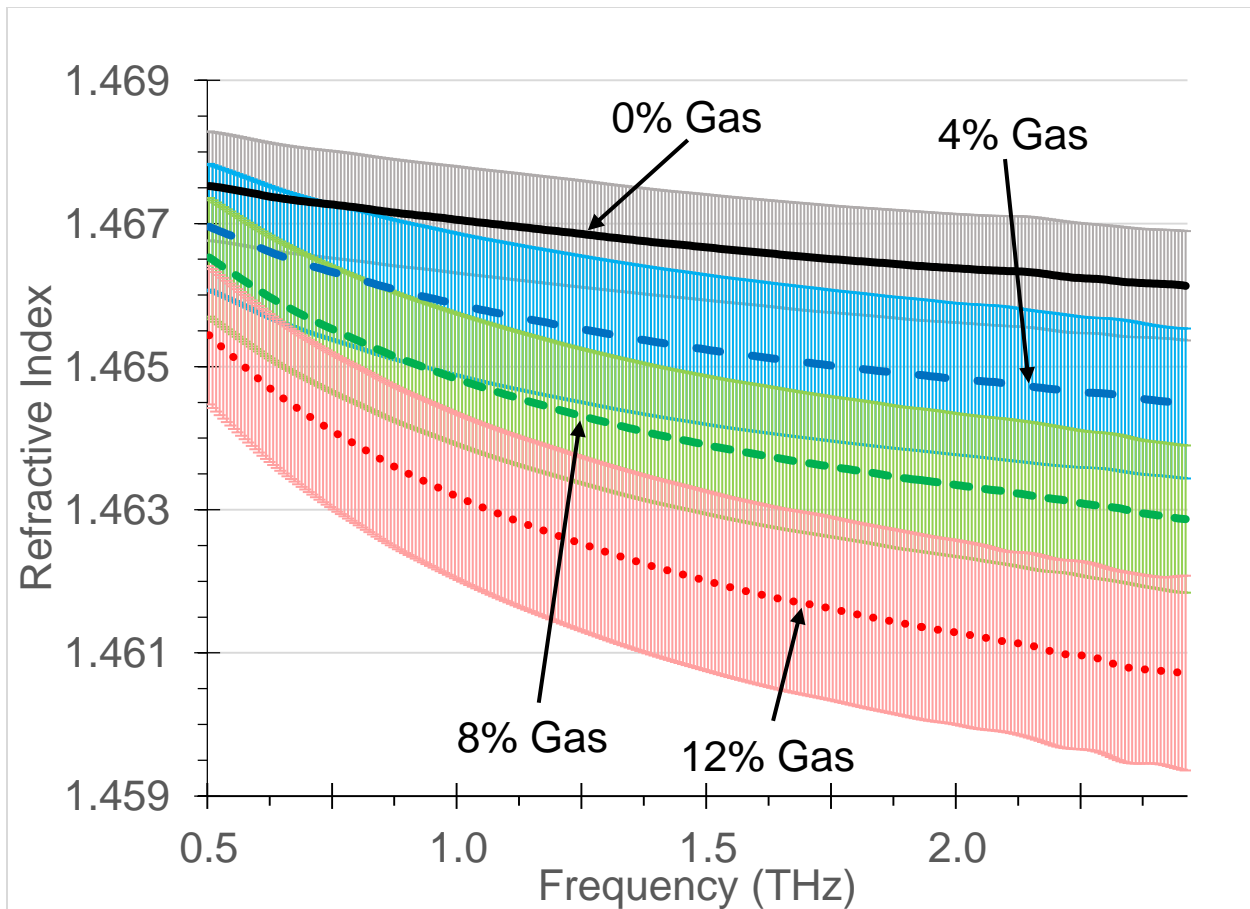


Figure 6. Mean refractive index from a single measurements of five cuvettes of gasoline engine oil (SAE 5W-20) samples with four levels of fuel contamination with 95% confidence interval bars.

Based on these results, the sampling method of a single measurement from five separate cuvettes did not yield results comparable to three consecutive measurements from a single cuvettes. While the latter method indicates potential, the former is indicative of the current state of the art.

### 3.2.2. Absorption Coefficient

The absorption coefficients for the four levels (0%, 4%, 8%, and 12%) of gasoline contaminated gasoline engine oil samples from all five cuvettes were illustrated in Fig. 7. The curves were similar to measurements from a single cuvette (Fig. 4) with noticeable spacing among the mean curves and ANOVA results indicated highly significant differences ( $p < 0.0001$ ) among the gasoline contamination levels across the entire 0.5-2.5 THz range. The mean absorption coefficients at 1.0 THz for the 0%, 4%, 8%, and 12% samples were 0.606, 1.018, 1.460, and 1.876, respectively with a standard deviations of up to 0.185. The 95% confidence interval bars were much longer for the contaminated samples (Fig. 7). Similar to the three measurements from a single cuvette each contamination level was significantly different from all of the others across the 0.5-2.5 THz range, based on Fisher's LSD method.

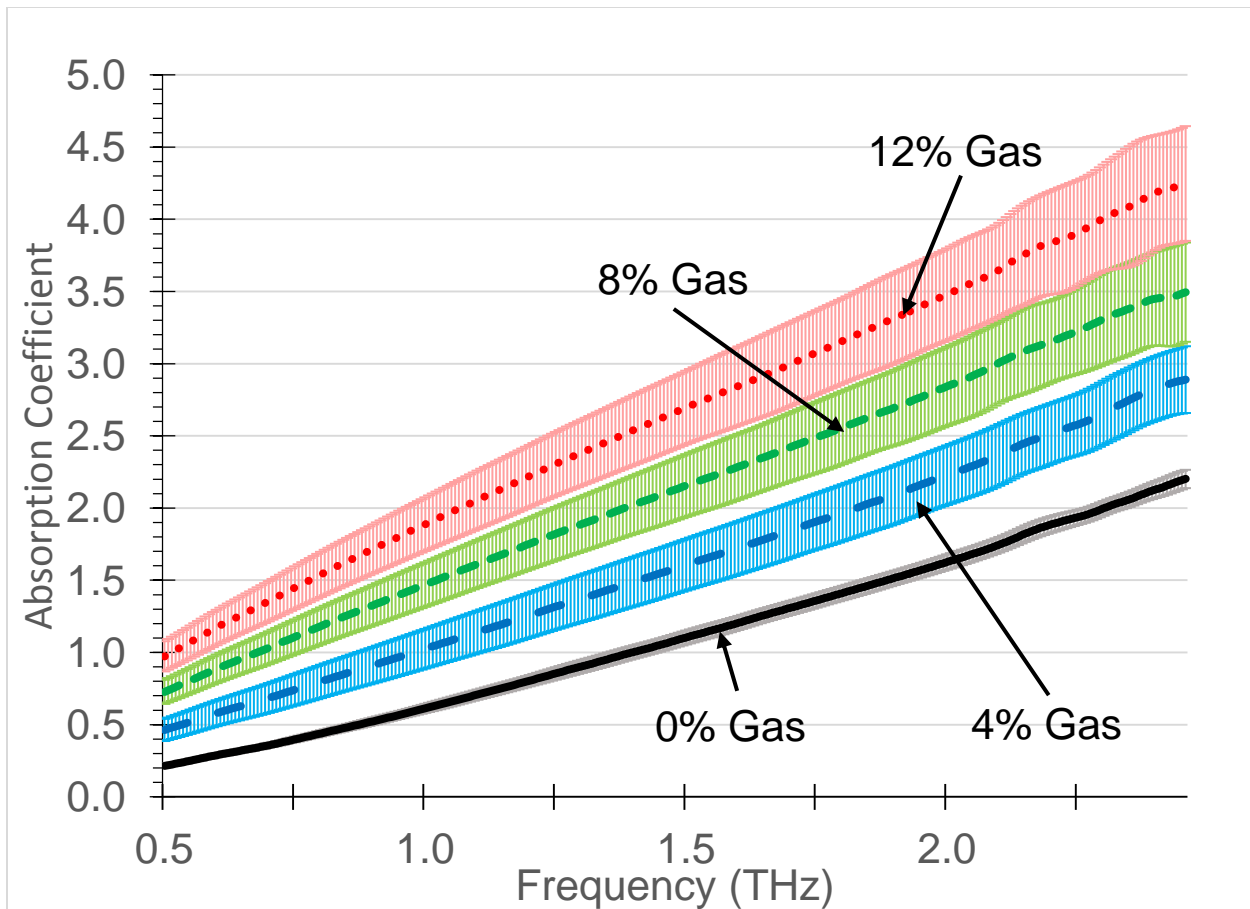


Figure 7. Mean absorption coefficient from a single measurement of five cuvettes of gasoline engine oil (SAE 5W-20) samples with four levels of fuel contamination with 95% confidence interval bars.

Based on these results, the sampling method of a single measurement from five separate cuvettes yielded results comparable to three consecutive measurements from a single cuvettes. The current state of the art was closer to potential than with refractive index measurements.

Further studies on the origin of the systematic errors may reduce the systematic error to the theoretical error level of thickness variations or at least to the smaller error level found with the 0% sample. So far, we cannot exclude that some of these errors are due to sample preparation (i.e. non-homogeneity) or contamination (i.e. gasoline attacking the PE windows of the cuvettes or temporary storage bottles).

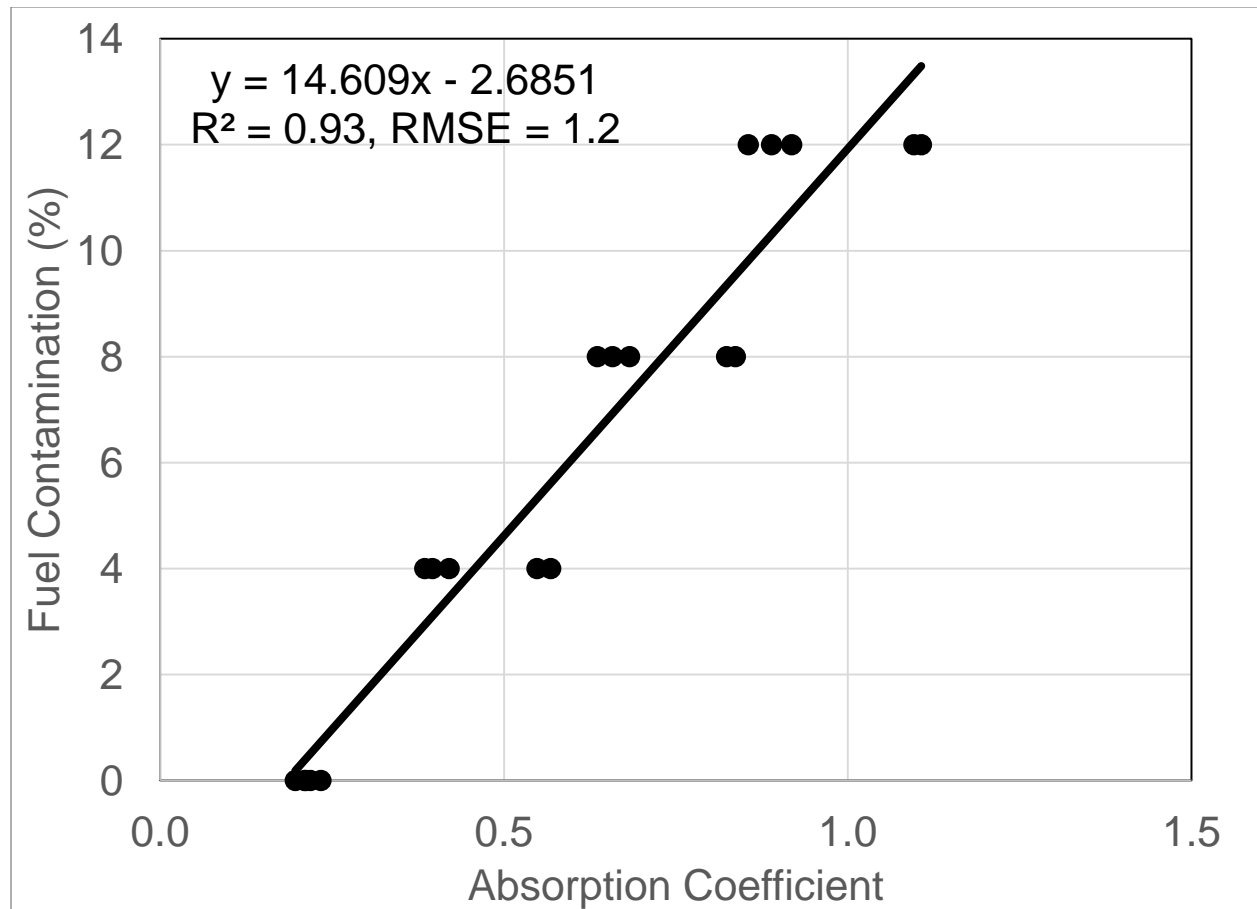
### 3.2.3. Absorption Coefficient as a Predictor of Gasoline Contamination

Regression was used with the data from the sampling method of a single measurement from five cuvettes. Based on the separation and statistical significance of means of each fuel contamination level for both refractive indices (Fig. 6) and absorption coefficients (Fig. 7), the absorption coefficient was of greater interest for predicting fuel contamination level. Data from nine frequencies (0.5-2.5 THz at 0.25 THz intervals) were used for linear regression analysis for

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4 absorption coefficient. All models were significant.  $R^2$  ranged from 0.93 at 0.5 THz down to 0.87  
5 at 2.5 THz. The 0.5 THz frequency was selected as the best model for absorption coefficient  
6 (Fig. 8). The linear equation at 0.5 THz for absorption coefficient predicting fuel contamination  
7 was:  
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$$\text{Fuel contamination (\%)} = -2.6851 + 14.609\alpha \quad (7)$$

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11  
12 This equation provided an preliminary estimate and the RMSE in predicting fuel contamination  
13 percentage was 1.2 percentage points. These measurements show that absorption coefficient with  
14 the five cuvette setups was able to differentiate between different contamination levels, but with  
15 some greater error than the fixed setup method.  
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Figure 8. Absorption coefficient from a single measurement of five cuvettes at 0.5 THz predicting fuel contamination with a linear model.

Regression equations from the sampling method of a single cuvette with three consecutive measurements yielded higher  $R^2$  values than from the five cuvettes with a single measurement. However, the later sampling method is a better indicator of results based on the current state of the art. Regardless, absorption coefficient of gasoline contaminated engine oil is a strong predictor of fuel contamination level, based on these experiments.

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4 **3.3 Delta Values Based on Five Cuvettes with a Single Measurement**  
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7 This method used data from the method of five cuvettes with a single THz-TDS measurement of  
8 each cuvette. Rather than using actual refractive index and absorption coefficient values as  
9 evaluation criteria, delta values were calculated by subtracting the value of the 0% sample from  
10 the respective 4%, 8%, and 12% contaminated sample values, reducing the influence of  
11 systematic errors. This subtraction can be understood as a calibration step as we are only  
12 interested in a change of the refractive index and absorption coefficient due to contamination  
13 with gasoline. All 0% samples were set to a delta value of zero.  
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16 **3.3.1. Delta Refractive Index**  
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18 The differences (deltas) in refractive indices for the four levels (0%, 4%, 8%, and 12%) of  
19 gasoline contaminated engine oil samples were illustrated in Fig. 9. The differences between the  
20 4%, 8%, and 12% samples and the 0% sample increased with contamination level and frequency.  
21 ANOVA results indicated significance among each of the gasoline contamination levels across  
22 the entire 0.5-2.5 THz range. However, the 95% confidence interval bars overlapped at lower  
23 frequencies. Based on Fisher's LSD method, each contamination level delta was significantly  
24 different from all of the others across the 1.23-2.5 THz range. The 12% sample was also  
25 significantly different from all the other samples across the 0.5-1.23 THz range. The non-  
26 contaminated sample was also significantly different from all other levels starting at 0.97 THz.  
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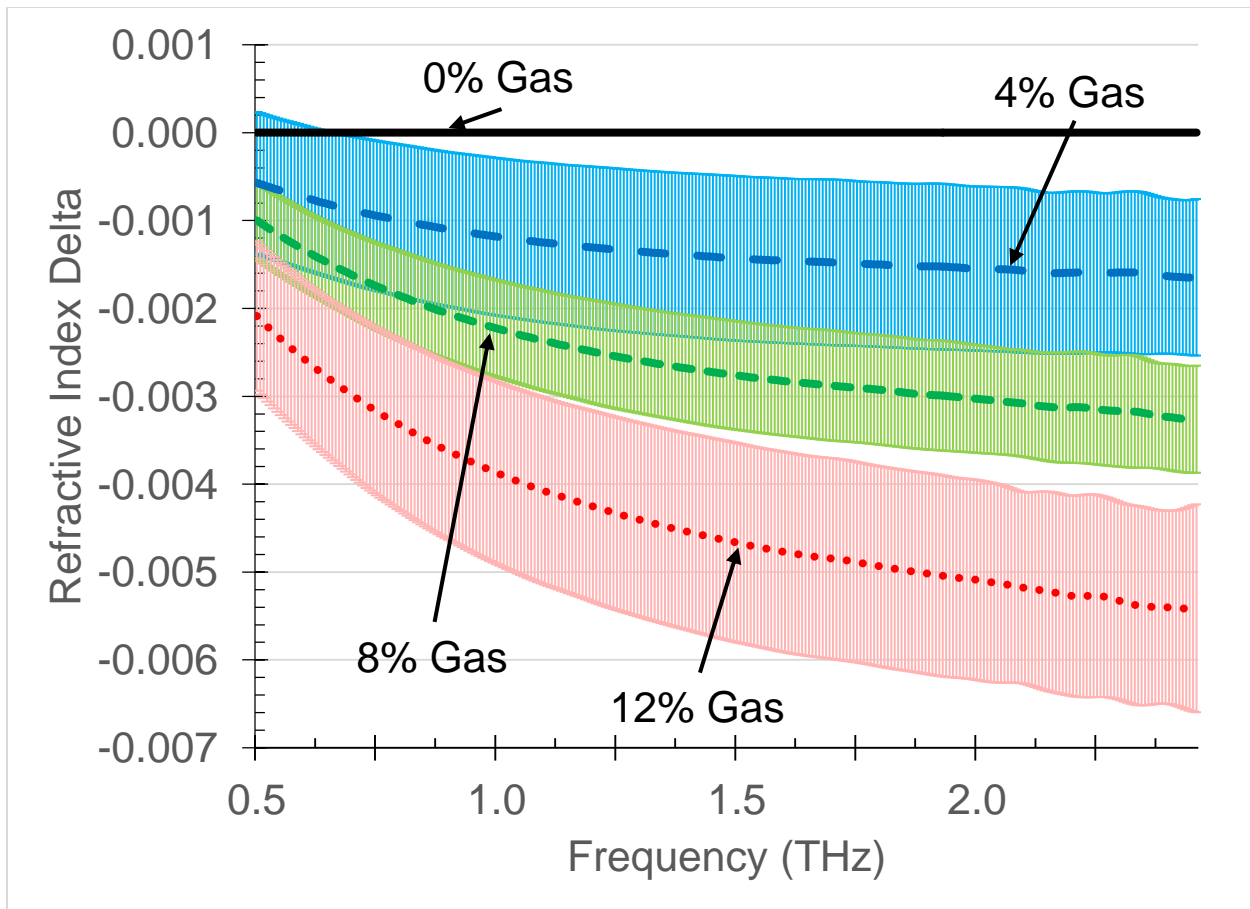


Figure 9. Mean delta of refractive index from a single measurements of five cuvettes of gasoline engine oil (SAE 5W-20) samples with four levels of fuel contamination with 95% confidence interval bars.

### 3.3.2. Delta Absorption Coefficient

The differences (deltas) in absorption coefficients for the four levels (0%, 4%, 8%, and 12%) of gasoline contaminated engine oil samples were illustrated in Fig. 10. The differences between the 4%, 8%, and 12% samples and the 0% sample generally increased with contamination level and frequency. ANOVA results indicated significance among each of the gasoline contamination levels across the entire 0.5-2.5 THz range. There was also distinction between the 95% confidence interval bars and based on Fisher's LSD method each contamination level delta was significantly different from all of the others across the entire 0.5-2.5 THz range.



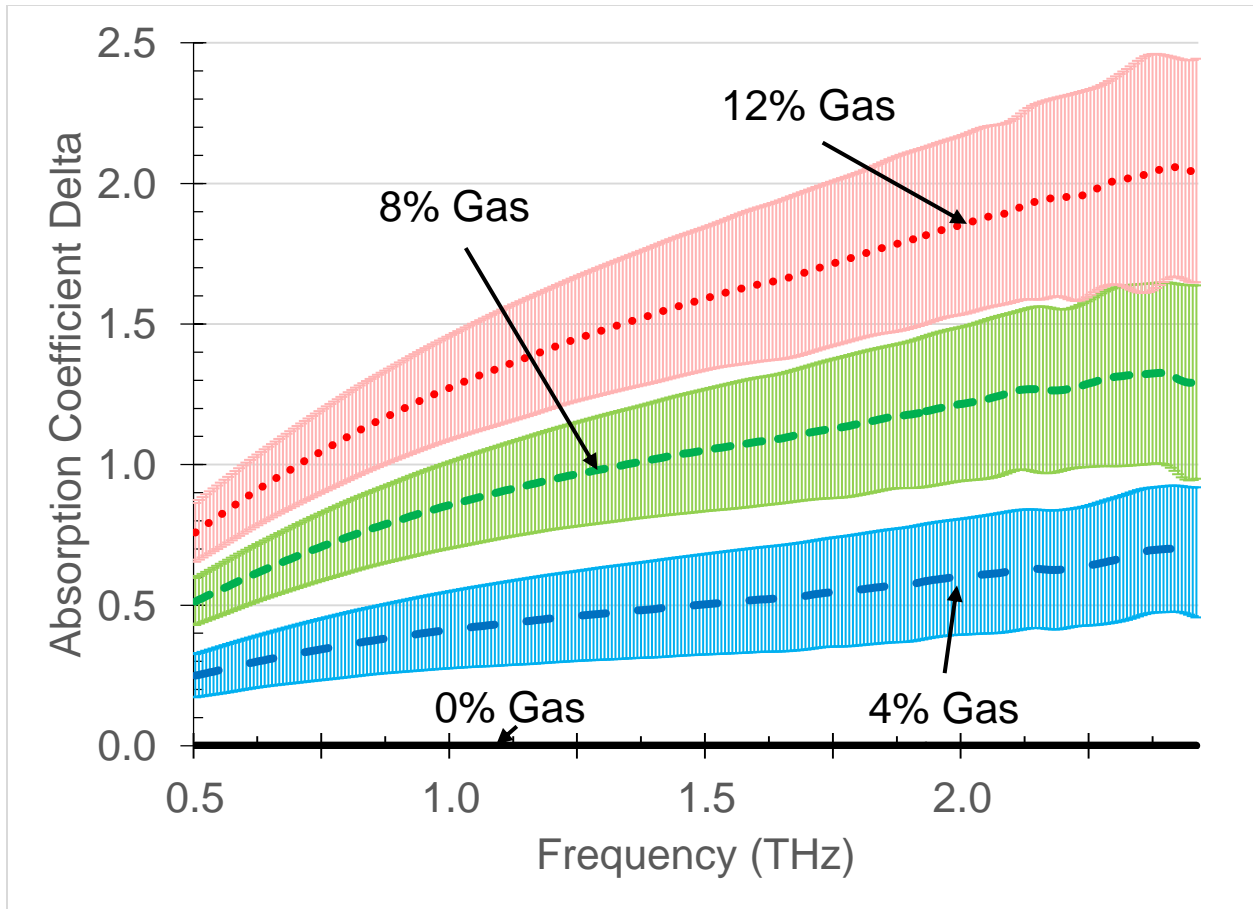


Figure 10. Mean delta of absorption coefficient from a single measurements of five cuvettes of gasoline engine oil (SAE 5W-20) samples with four levels of fuel contamination with 95% confidence interval bars.

### 3.3.3. Delta Absorption Coefficient as a Predictor of Gasoline Contamination

The delta data was also fitted with regression. Based on the separation and statistical significance of means of each fuel contamination level, the delta absorption coefficient was preferred for predicting fuel contamination level. Data from nine frequencies (0.5-2.5 THz at 0.25 THz intervals) were used for linear regression analysis for delta absorption coefficient. All models were significant, with  $R^2$  ranging from 0.93 at 0.5 THz down to 0.88 at 2.5 THz. The 0.5 THz frequency was selected as the best model for delta absorption coefficient models (Fig. 11). The linear equation at 0.5 THz for delta absorption coefficient predicting fuel contamination was:

$$\text{Fuel contamination (\%)} = 0.4369 + 14.626\Delta\alpha \quad (8)$$

This estimate of the relationship of delta absorption coefficient to fuel contamination (Eq. 11) resulted in a RMSE of 1.2 percentage points in predicting fuel contamination percentage. The delta measurement method performed similar to the five cuvette setups and was able to differentiate among contamination levels.

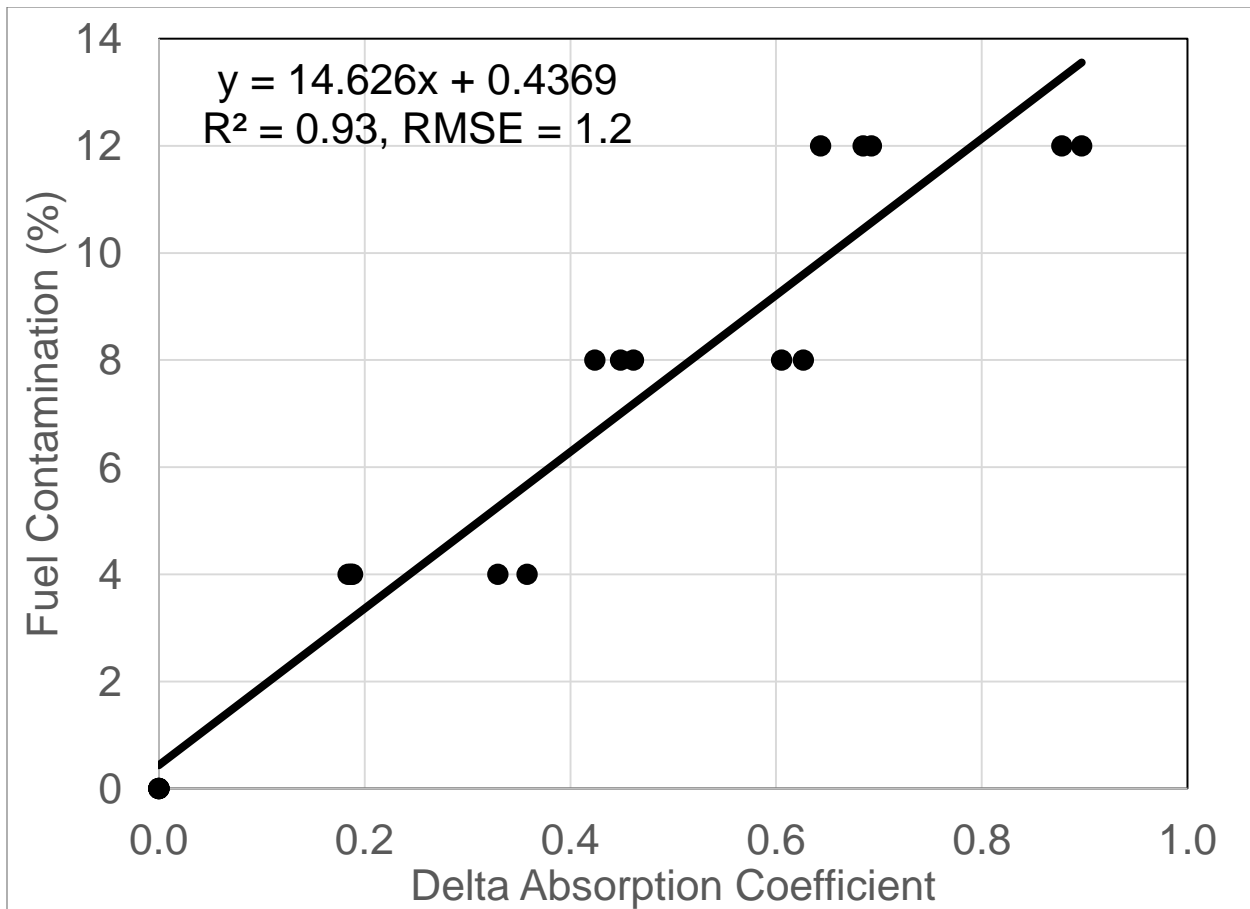


Figure 11. Delta absorption coefficient from a single measurement of five cuvettes at 0.5 THz predicting fuel contamination with a linear model.

### 3.4 Summary Discussion

Based on this study, THz-TDS has potential for identifying gasoline contamination and possibly other contaminants in engine oil. One challenge is calibration among THz-TDS setups and measurement methods. By using the same cuvette and measurement delta, calibration differences may be inconsequential.

We investigated systematic errors due to variations in the measurement technique such as probe volume and alignment of the THz setup by recording five individual cuvette measurements with sample thicknesses of 5 mm, 10 mm, and 15 mm. This shows that systematic errors introduced by variation of the setup can be tolerated, showing the high potential of this measurement technique. Further studies on the origin of the systematic errors may reduce the systematic error to the theoretical error level of thickness variations or at least to the smaller error level found with the 0% sample.

Gasoline contamination has been reported to reduce oil viscosity [3, 4, 5]. However the refractive index and absorption coefficient changes with increased gasoline contamination differed from those of oil of different viscosities. Based on the THz-TDS measurements of three oil viscosities, refractive index and absorption coefficient generally increased with viscosity [28].

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4 In this study, refractive index decreased and absorption coefficient increased with gasoline  
5 contamination. While the increase in gasoline contamination presumably resulted in lower  
6 viscosity, THz-TDS detected a change in the gasoline contaminated oil that was independent of  
7 viscosity change.  
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10 Engine oil regularly reaches temperatures of 100°C, with changes including reduced viscosity  
11 and increased oxidation. This study focused on gasoline contamination and excluded other  
12 potential changes due to heating of the contaminated oil. Further studies are recommended to  
13 determine if THz-TDS is as effective at identifying gasoline contamination in oil at normal  
14 operating temperatures.  
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17 Sensors have been developed for engine oil [14, 10, 36] that used oil viscosity as a proxy for  
18 gasoline fuel contamination, rather than measuring fuel content directly. Normal engine  
19 operating conditions result in oil oxidation which increases viscosity, so fuel dilution could be  
20 underestimated due to oil oxidation. As modern spark ignition engines increase the use of direct  
21 fuel injection with associated increase in fuel dilution of oil [9] a more direct means of  
22 measuring fuel contamination may be needed. Further experiments could verify the relationships  
23 of THz-TDS measurements among gasoline contamination which reduces viscosity and oil  
24 viscosity differences or other factors that impact oil viscosity. While THz-TDS is far from  
25 widespread deployment as a method of identifying engine oil contaminants, it has potential and  
26 deserves further investigation.  
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#### 30 **4. Conclusions**

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33 Gasoline engine oil (SAE 5W-20) was contaminated with four levels (0%, 4%, 8% and 12%) of  
34 gasoline fuel and submitted to THz-TDS measurement. Refractive index decreased with  
35 increased fuel contamination and absorption coefficient increased with increased fuel  
36 contamination.  
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39 The single cuvette with three consecutive measurements illustrated the potential of THz-TDS  
40 when a fixed setup is used, such as a potential miniaturized setup installed in an engine. For both  
41 refractive index and absorption coefficient there were highly significant differences ( $p < 0.0001$ )  
42 among each of the gasoline contaminant levels across the 0.5-2.5 THz range. The 2.5 THz  
43 frequency was the best to predict fuel contamination based on refractive index and 0.5 THz was  
44 the best frequency for absorption coefficient with  $R^2$  values of 0.987 and 0.998 and RMSE of  
45 0.51 and 0.21, respectively.  
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48 Measurements from five separate cuvettes estimated differences based on probe volume and  
49 alignment differences of THz setups. For absorption coefficient the four contamination levels  
50 were significantly different from each other at each frequency. Absorption coefficient best  
51 predicted gasoline contamination at 0.5 THz with a  $R^2$  of 0.93 and RMSE of 1.2 percentage  
52 points.  
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55 The delta values from the five individual cuvette measurements improved the ability to  
56 distinguish contamination levels. Each refractive index contamination level delta was  
57 significantly different from all of the others across the 1.23-2.5 THz range. For absorption  
58 coefficient each contamination level delta was significantly different from all of the others across  
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4 the entire 0.5-2.5 THz range. The 0.5 THz frequency has the highest  $R^2$  of 0.93 in predicting fuel  
5 contamination based on absorption coefficient, translating to an RMSE in gasoline contamination  
6 of 1.2 percentage points.  
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9 THz-TDS demonstrated high potential for distinguishing gasoline fuel contamination. Based on  
10 this study, continued exploration of THz-TDS for engine oil contaminants is warranted to  
11 determine the extent of the THz-TDS potential to distinguish other engine oil contaminants.  
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